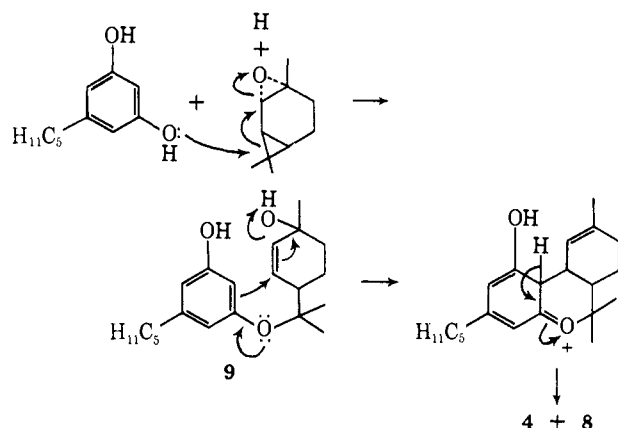


fonic acid, whereas it was *ca.* 0.6 (*i.e.*, increase of *cis* products) with the use of boron trifluoride etherate. We interpret these results as suggesting that *trans*- and *cis*- Δ^1 -TNCs are first formed (Scheme II) and are then

Scheme II



converted into their transformation products 3 and $5 \rightarrow 7$, respectively. This is in complete agreement with the known acid-catalyzed transformations in cannabinoids.^{1,12} Furthermore, the results suggest that the reaction has a more concerted character when a nonprotonic acid catalyst like BF_3 is used, whereas acid catalysts like *p*-TSA, which give a more carbonium ion character to the allylic system in the intermediate 9 , give the *trans* products, which are more thermodynamically and kinetically stable.^{1,2}

Further work along these lines is in progress and will be the subject of future communications.

Acknowledgment. The authors wish to thank Dr. R. Lyle for helpful discussions and for obtaining the ORD curves and Dr. L. Mir for carrying out the preparative vpc. This work was carried out with the support of Contract No. PH-43-68-1339, National Institute of Mental Health.

(12) B. Yagen and R. Mechoulam, *Tetrahedron Lett.*, 5353 (1969).
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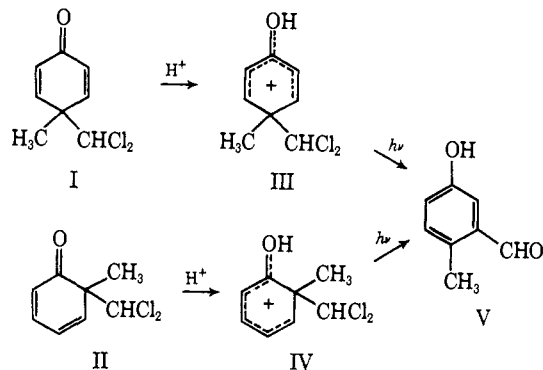
Photochemical Rearrangement of Cyclohexadienyl Cations

Sir:

In the presence of sulfuric acid, 4,4-dimethyl- and 4,4-diphenyl-substituted cyclohexa-2,5-dienones readily undergo the dienone-phenol rearrangement.¹ In contrast, the "abnormal Reimer-Tieman" dienones 4-methyl-4-dichloromethylcyclohexa-2,5-dienone (I) and 6-methyl-6-dichloromethylcyclohexa-2,4-dienone (II) do not rearrange under similar conditions.² Furthermore, they can be recovered quantitatively from concentrated sulfuric acid by dilution with water,³ in spite of the

(1) (a) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **29**, 509 (1964); (b) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); (c) A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 207 (1966).
(2) K. v. Anwers and G. Keil, *Ber.*, **35**, 4207 (1902).

fact that their uv-visible and nmr spectra clearly indicate the formation of the ionic species responsible for the normal rearrangement, the oxygen-protonated, de-



localized cyclohexadienyl cations III and IV, respectively.^{4,5} Only heating at 60° for 24 hr causes partial 1,2 migration of the methyl group in I and generates, after hydrolysis, 2-methyl-4-hydroxybenzaldehyde.⁶

In the present communication we report the efficient photorearrangement of ions III and IV to the same photoproduct, 2-methyl-5-hydroxybenzaldehyde (V).

Figures 1 and 2 show successive changes in the uv-visible absorption spectra of IV and III following short-duration irradiations⁷ with light of 370 and 262 nm, respectively, at ambient temperature. Figure 1a illustrates the gradual disappearance of IV (λ_{max} 370 nm) with simultaneous increase in absorbance at 258 and 298 nm. That these two absorption bands do not belong to the same species is shown by the subsequent changes shown in Figure 1b. Thus the peak at 298 nm continues to increase upon further irradiation whereas that at 258 nm gradually decreases after reaching a maximum. The final product (λ_{max} 298 and 388 nm) seems to be photostable. The absorption spectrum of a solution of IV irradiated to any per cent conversion remained unchanged after standing in the dark for extended times. This testifies that the changes in Figure 1 are photochemical with no interference from thermal reactions. It is quite clear that ion IV is converted photochemically to an intermediate species (λ_{max} 258 nm) which in turn undergoes photolysis to a product absorbing at λ_{max} 298 nm. The three isosbestic points at 248, 272, and 332 nm in Figure 1b indicate that the intermediate \rightarrow product photoconversion preserves a constant stoichiometry and that the transformation is void of competitive or consecutive slow reactions. On the other hand the isosbestic point at 329 nm in Figure 1a merely indicates a coincidental equality of extinction coefficients at that wavelength for the three species present.

Figure 2 shows changes in the absorption spectrum of III on irradiation at 262 nm. Again the photoreaction is quite clean and the final product exhibits a uv-visible spectrum (λ_{max} 298 and 388 nm) indistinguishable from that obtained from IV.

Preparative-scale photolysis of either III or IV 10^{-2} M in 96% H_2SO_4 at 17° was accompanied by HCl liber-

(3) H. Budzikiewicz, *Tetrahedron Lett.*, 12 (1960).

(4) E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968).

(5) V. P. Vitullo, *ibid.*, **34**, 224 (1969).

(6) T. G. Miller, *ibid.*, **27**, 1549 (1962).

(7) Bausch & Lomb high intensity monochromator with 125-W high-pressure Hg arc.

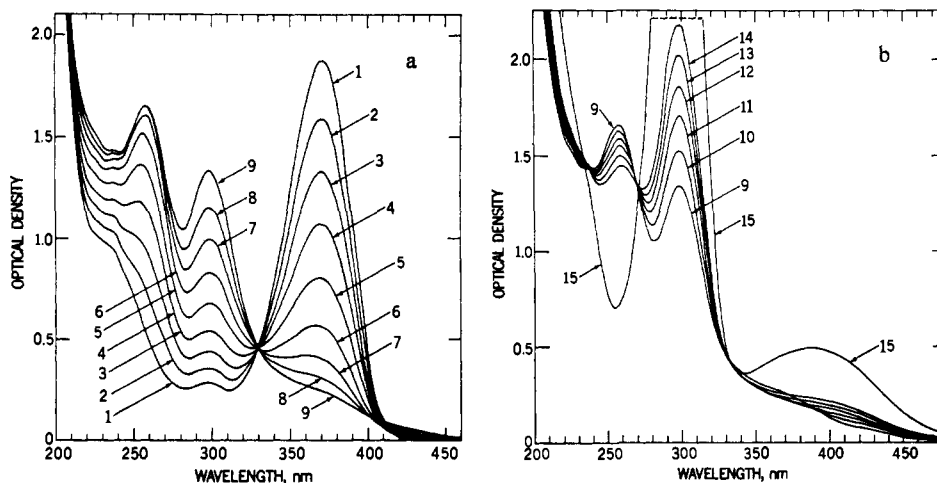
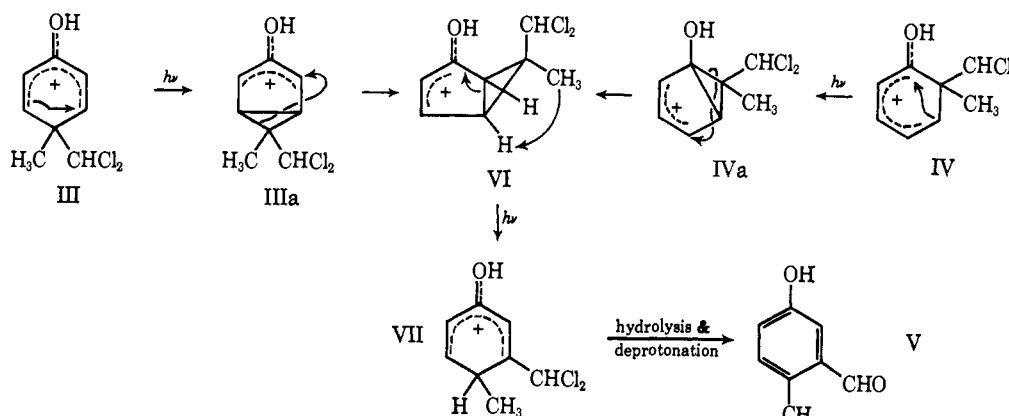


Figure 1. Uv-visible absorption spectrum of IV in 96% H_2SO_4 : 1, before irradiation; 2-14, after consecutive 5-sec irradiations at 370 nm; and 15, after a total of 4 min of irradiation.

ation and led to the isolation of previously unreported V: mp 114-115°; 2,4-DNP, 238°; uv (CH_3OH) λ_{max} 222 nm (ϵ 13,690), 225 (6050), 325 (3120); (H_2SO_4) λ_{max} 298 nm (11,480). The ir spectrum of V showed absorptions characteristic of carbonyl and nonintramolecular hydrogen-bonded OH. The nmr spectrum (acetone- d_6 , 60 Mcps) confirmed these assignments (OH variable with concentration,⁸ aldehyde proton singlet δ 10.2 ppm) and showed one aromatic proton (δ 7.3 ppm) deshielded relative to the main aromatic complex (2 H, δ 7.0 ppm). This places the methyl and carbonyl groups ortho to each other. Of the two possible methylhydroxybenzaldehyde structures consistent with the above data, 2-methyl-5-hydroxybenzaldehyde and 2-methyl-4-hydroxybenzaldehyde, the latter was eliminated on the basis of mixture melting point and infrared spectra comparison.

The photorearrangement of either III or IV to protonated V is consistent with the mechanism in Scheme I. The initial 3,5 (or 1,5) bonding leading to IIIa (or IVa) is predicted to be conrotatory—and thus sterically precluded—in the ground state but disro-

Scheme I



tatory—and allowed—in the first excited state of III (or IV).⁹ Indeed, similar bonding has been observed

(8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, p 215.

(9) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

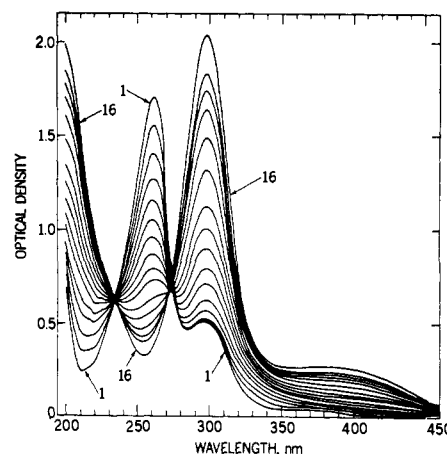


Figure 2. Uv-visible absorption spectrum of III in 96% H_2SO_4 : 1, before irradiation; 2-16, after consecutive 5-sec irradiation at 262 nm.

to take place efficiently in the photolysis of polymethyl-substituted benzenonium ions.^{10,11}

Unlike the results of Swatton and Hart¹² who observed cyclopropane migration in hydroxyhexamethylbicyclohexenyl cation at room temperature, no similar

(10) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 7144 (1968).

(11) R. F. Childs and S. Winstein, *ibid.*, 90, 7146 (1968).

(12) D. W. Swatton and H. Hart, *ibid.*, 89, 5075 (1967).

scrambling seems to take place in ions IIIa and IVa. This is suggested by the fact that quenching experiments prior to complete photoconversion of either III or IV failed to yield any neutral dienone other than the original one. A IIIa \rightleftharpoons VI \rightleftharpoons IVa equilibrium would be detected in the recovered neutral dienones. Since the rate of cyclopropane migration is very sensitive to the electron-donating ability of substituents on the cyclopropane bridge,¹¹ it is conceivable that the electron-withdrawing effects of the dichloromethyl group forces the thermal conversion of both IIIa and IVa entirely in the direction of VI, the most stable cation.¹³

The fact that both III and IV yield the same photo-product strongly supports the suggestion of a common intermediate in both reactions. The absorption band centered at 258 nm in Figures 1a and 1b was associated with this intermediate, ion VI. Its presence in the III \rightarrow V photoconversion (Figure 2) would be masked by the absorption of III. Furthermore, since the excitation light would be strongly absorbed by the intermediate, its concentration would remain small due to efficient conversion to V. The identity of VI is suggested by the isolation of bicyclo[3.1.0]hex-3-en-2-ones from photochemical rearrangements of other cyclohexadienones¹⁴ and by the stabilizing effect of the CHCl₂ group in ion VI against thermal rearrangement. Since all spectra in Figures 1 and 2 remain unchanged in the dark it is obvious that an additional photon is required for rearrangement to VII.

The photoconversion of VI to VII is readily understood (see Scheme I). Theoretically, cyclopropane opening and methyl 1,2 migration can take place in the alternative direction to yield eventually 2-methyl-3-hydroxybenzaldehyde. The fact that none was isolated is consistent with the previous observed dependence of isomer distribution on acidity.¹⁵

Acknowledgment. This work was supported by National Aeronautics and Space Administration Grant No. NGL-09-010-008. Financial assistance from The Research Committee of George Washington University is also gratefully acknowledged.

(13) Admittedly, hydrolysis of the dichloromethyl group could take place prior to formation of VII. The sequence shown is suggested by the known susceptibility of the CHCl₂ group toward hydrolysis when attached to an aromatic residue and the contrasting stability when connected to an alkyl moiety.

(14) P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967.

(15) H. E. Zimmerman, R. Keese, J. Nasielski, and J. W. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(16) Postdoctoral Research Scientist, 1969-1970.

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The Antipolar Mechanism of Thermal Allylic Rearrangements

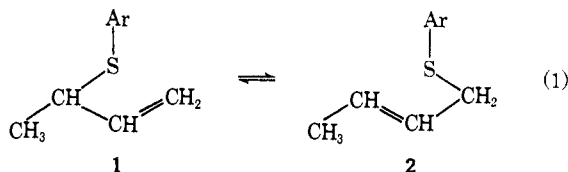
Sir:

A striking example of 1,3-sigmatropic rearrangement¹ where a p orbital is binding the migrating group to the carbon skeleton² appears to have been established³

(1) See for full discussion, R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

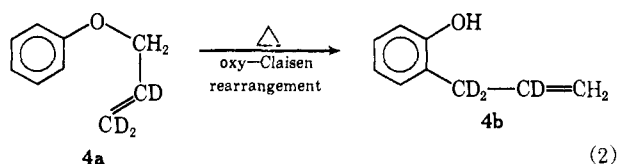
for triallylboron ($E_a \cong 11$ kcal/mol). While it is possible that this does not qualify as a concerted process because it may involve a zwitterionic intermediate, it cannot be classified with mechanisms analogous to solvolytic allylic rearrangement, where an ion pair intermediate is formed.

A thioallylic rearrangement (eq 1) which is formally analogous to the triallylboron rearrangement has been previously invoked by us⁴ to explain the course of the thio-Claisen rearrangement of **1** and **2** (and related compounds). This observation has been recently confirmed by others⁵ studying the thermolysis of α -methylallyl 2-quinolyl sulfides. We are now able to



discuss our studies of the thioallylic rearrangement of allyl aryl sulfides which suggest that the reaction course is unprecedented among allylic rearrangements⁶ and warrants reexamination of the evidence upon which previous reports^{3,7} of such thermally induced reactions have been based.

Support for this claim stems from the synthesis of the appropriately deuterated allyl phenyl sulfide **3a** (C₆H₅-S-CD₂-CH=CH₂). The rate of its isomerization to the isotopic equilibrium composition (eq 3) could be readily pursued by nmr, and the activation parameters determined in this manner for reaction in a wide variety of solvent media are listed in the Table I. On the other hand, an oxygen analog of **1** (namely **4a**) showed no change of constitution after more than 5 hr of heating at 160°. Moreover, when this deuterated phenyl allyl ether was heated at 195° for 16 hr, the only product of Claisen rearrangement (eq 2) was **4b**, indicating that even at the elevated temperatures, no (prior) thermal oxyallylic rearrangement⁸ had taken place.



The photooxyallylic rearrangement at ambient temperatures also could not be realized. Thus, when a

(2) J. A. Berson, *ibid.*, **1**, 152 (1968).

(3) B. M. Mikhailov, V. S. Bogdonov, G. V. Lagodzinskaya, and V. G. Pozdnev, *Chem. Abstr.*, **65**, 595c (1966).

(4) H. Kwart and M. H. Cohen, *Chem. Commun.*, 319 (1968). This rearrangement (eq 1) had been previously investigated by A. C. Cope, D. E. Morrison, and L. Field (*J. Amer. Chem. Soc.*, **72**, 59 (1950)) and declared to have failed. We now can report direct measurement of the rate of rearrangement by glc separation of **1** and **2**. A full account of this work is being prepared for publication.

(5) Y. Makisumi and A. Murabayashi, *Tetrahedron Lett.*, 1975 (1969).

(6) E. A. Braude, *Quart. Rev., Chem. Soc.*, **4**, 404 (1950).

(7) M. Leguan, G. Guillermin, and A. Jean, *C. R. Acad. Sci., Ser. C*, **268**, 1542 (1969).

(8) Under more severe conditions γ -¹⁴C allyl ether of 2,4,6-trimethylphenol experiences some distribution of its radioactivity between the α and γ carbons of the allyl group. This result was accounted for, not by an assumed oxyallylic rearrangement, but rather *via* a stepwise ortho-ortho rearrangement which is disallowed by the Woodward-Hoffmann selection rules;¹ see P. Fahrni and H. Schmid, *Helv. Chim. Acta*, **42**, 1102 (1959).